ISSN 1062-8738, Bulletin of the Russian Academy of Sciences: Physics, 2017, Vol. 81, No. 7, pp. 817–821. © Allerton Press, Inc., 2017.
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Mössbauer Study of Products of the Thermocatalytic Treatment of Kerogen-Containing Rocks

A. G. Ivanova[a, *], A. V. Vakhin[b], E. V. Voronina[a], A. V. Pyataev[a], D. K. Nurgaliev[b], and S. A. Sitnov[b]

[a] *Institute of Physics, Kazan Federal University, Kazan, 420008 Russia*

[b] *Institute of Geology and Petroleum Technologies, Kazan Federal University, Kazan, 420008 Russia*

**e-mail: 19ivanova91@gmail.com*

Abstract—To understand the mechanism of highly efficient catalyst formation from precursors, the active form of an iron-containing catalyst and kerogen samples from the Bazhen formation are studied by Mössbauer spectroscopy and X-ray diffraction analysis. It is established that as a result of phase changes, the multicomponent precursors are transformed into mixed transition metal oxides. It is found that the thermocatalytic effect on pyrite-containing kerogen leads to the formation of pyrrhotite FeS_{1-x} and mixed oxides of iron.

DOI: 10.3103/S1062873817070139

INTRODUCTION

To satisfy our ever-growing need for energy, and because of the change in the structure of oil reserves with an prevailing part of heavy hydrocarbon raw materials, the oil industry is focusing on nontraditional and hard-to-reach hydrocarbons. Under the conditions of the depletion of our traditional energy reserves, high-viscosity bituminous and shale oil are acquiring new importance [1]. In order to improve oil recovery, it is of interest to study the hydrothermal processes that act on a deposit [2, 3]. For example, exposure to steam and heat enables us to change the rheological properties and improve the characteristics of extracted oil [4]. It is therefore important to create highly active catalysts, both oil- and water-soluble, and heterogeneous nanosized oxide systems that increase the effectiveness of steam–heat treatment [5]. Combustible oil-bearing shale ("immature" oil) or kerogen may be considered sources of profitable hydrocarbon production, provided that modern technologies are used. Among the technologies for developing kerogen deposits, researchers are focusing on the thermal destruction of kerogen directly in a reservoir using the technique of in-situ retorting, which leads to the formation of so-called synthetic oil [6]. One way of intensifying intra-layer transformations of kerogen is to use nanoscale catalysts based on transition elements. Metals of the iron group are being investigated for use in the in-situ upgrading of heavy oil. In addition, iron is present in such formations as part of different compounds.

To devise technological solutions and create various agents for pumping into a reservoir under development, we must study the structural-phase changes of iron-containing components of oil and kerogen in the presence of catalysts and their precursors at the relatively low temperatures maintained in productive reservoirs using thermal technologies. To identify and establish the mechanism behind the formation of a highly efficient catalyst from precursors directly in a formation, we studied the active forms of iron-containing catalysts and samples of kerogen rocks from the Bazhen formation.

EXPERIMENTAL

Laboratory simulations of thermocatalytic exposure were conducted in a high-pressure reactor (volume, 300 cm^3) (Parr Instruments, United States) under variety of conditions that depended on the selected objects of study.

The objects of our investigation were products of the thermobaric effect on a model system (300°C and a pressure of 8.6 MPA) containing a mixture of water and high-viscosity oil from the Ashalchinskoye deposit in the Republic of Tatarstan and a catalyst precursor in an inert gas atmosphere (nitrogen) for 6 h. Iron resinate (for sample 1) and a mechanical mixture of iron resinate and nickel resinate (for sample 2) were used in a 1 : 1 weight ratio as catalyst precursors. The latter were obtained on the basis of tall oil and sulfates of the corresponding metals. Samples 1 and 2 were obtained from precursors as a result of thermobaric exposure.

A product of the thermocatalytic effect on a kerogen sample from the Bazhen formation (operating pressure, 5.0 MPa; temperature, 300°C; duration of the experiment in the operating mode, 6 h) also served as an object of study (sample 3) (as a molecular precursor, cobalt carboxylate was chosen as the catalytic agent).

Kerogen was isolated by successively treating debituminized ground rock with solutions of hydrochloric and hydrofluoric acids. Pyrite bound with kerogen in a